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(54) NONAQUEOUS BATTERY

(57)Abstract:

PURPOSE: To reduce rise in internal resistance of a battery and to provide excellent shelf life at high temperature.

CONSTITUTION: A nonaqueous battery is provided with a negative electrode employing lithium as a negative electrode active material and a positive electrode employing lithium-transition metals composite oxides shown by a formula $\text{Li}_X\text{Ni}_{1-Y}\text{M}_Y\text{O}_Z$ ($0 < X < 1.3$, $0 \leq Y \leq 1.8$, $2 < Z < 2.2$, and M represents cobalt or two or more kinds of transition metals including cobalt) as a positive electrode active material. To the positive electrode active material, 0.1-20 mole % of nickel oxide, in which the oxidation numbers of nickel is three or less and lithium is not contained in a crystal, and/or cobalt oxide, in which the oxidation numbers of cobalt is three or less and lithium is not contained in a crystal, is/are added. In this way, decomposition of an electrolyte in high temperature storage is suppressed by adding the nickel oxide and/or the cobalt oxide to the positive electrode active material.

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CLAIMS

[Claim(s)]

[Claim 1] The negative electrode which uses a lithium as a negative-electrode active material, and formula:LiX nickel1-Y MY OZ however, it is $0 < X < 1.3$, $0 \leq Y \leq 1$, and $1.8 < Z < 2.2$, and M is two or more sorts of transition metals containing cobalt or cobalt -- In a nonaqueous cell equipped with the positive electrode which uses the lithium-transition-metals multiple oxide expressed as positive active material the cobalt oxide with which the oxidation number of the nickel oxide with which the oxidation number of nickel does not contain a lithium in a crystal or less by three, and/or cobalt does not contain a lithium in a crystal or less by three to said positive active material -- 0.1-20-mol % -- the nonaqueous cell characterized by being added.

[Claim 2] The nonaqueous cell according to claim 1 said whose nickel oxide is NiO.

[Claim 3] said cobalt oxide -- Co 3O4 it is -- nonaqueous cell according to claim 1.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to amelioration of the positive electrode aiming at improving the hot preservation property of a nonaqueous cell in detail with respect to a nonaqueous cell.

[0002]

[Description of the Prior Art] In recent years, the nonaqueous cell which uses a metal lithium or a lithium ion as a negative-electrode ingredient for occlusion, the alloy which may be emitted, or a carbon material, and uses a lithium-transition-metals multiple oxide as a positive-electrode ingredient is attracting attention as a cell which has a high energy consistency.

[0003] As the above-mentioned lithium-transition-metals multiple oxide, they are LiMnO₂ and LiFeO₂. Although it reaches and LiX nickel1-Y CoY OZ etc. is known well (however, $0 < X < 1.3$, $0 \leq Y \leq 1$, $1.8 < Z < 2.2$), it is LiX nickel1-Y CoY OZ especially.

Capacity is large and it is one of the positive active material which attracts attention most. [0004] However, LiX nickel1-Y CoY OZ If the nonaqueous cell used as positive active material is saved at an elevated temperature for a long period of time or is saved at an elevated temperature for a long period of time by the condition after charge (condition that the lithium ion was emitted from positive active material) especially in the case of a rechargeable battery, the internal resistance of a cell will rise. Thus, it is considered to be based on the following reason that internal resistance rises.

[0005] Namely, at the time of charge of a rechargeable battery, the lithium was emitted from the above-mentioned positive active material, and the nickel in an active material or the oxidation number of cobalt exceeded 3 after charge, and the nickel in an active material or the oxidation number of cobalt is over 3 also at the time of discharge. Furthermore, also in a primary cell, the nickel in an active material or the oxidation number of cobalt may exceed 3 in early stages of discharge. Thus, if the oxidation

number of nickel or cobalt exceeds 3, the electrolytic solution decomposes by the catalysis of such positive active material, gas occurs, by this gas that occurred, deformation will take place to the plate configuration of a positive electrode, the adhesion of a positive-active-material layer and an axis (charge collector) will fall, and internal resistance will rise.

[0006] Thus, since there was a problem that it was unsuitable for the nonaqueous cell which used this kind of positive active material as a power source of the land mobile radiotelephone left under an elevated temperature for a long period of time, that improvement was demanded.

[0007] The place which this invention is made so that it may meet this request, and is made into the purpose is LiX nickel1-Y CoY OZ excellent in the elevated-temperature preservation property. It is in offering the nonaqueous cell used as positive active material.

[0008]

[Means for Solving the Problem] The nonaqueous cell (the "this invention cell" is called below.) concerning this invention for attaining the above-mentioned purpose The negative electrode which uses a lithium as a negative-electrode active material, and formula:LiX nickel1-Y MY OZ (however, it is $0 < X < 1.3$, $0 \leq Y \leq 1$, and $1.8 < Z < 2.2$, and M is two or more sorts of transition metals containing cobalt or cobalt.) In a nonaqueous cell equipped with the positive electrode which uses the lithium-transition-metals multiple oxide expressed as positive active material the cobalt oxide with which the oxidation number of the nickel oxide with which the oxidation number of nickel does not contain a lithium in a crystal or less by three, and/or cobalt does not contain a lithium in a crystal or less by three to said positive active material -- 0.1-20-mol % -- it is added and changes.

[0009] As for the nickel oxide and cobalt oxide in this invention, those oxidation numbers are limited to three or less thing. It is because it has the catalysis to which, as for this, the oxidation number exceeds 3 and to which NiO₂ (the oxidation number of nickel: 4) produced electrochemically, CoO₂, etc. promote disassembly of the electrolytic solution (the oxidation number of cobalt: 4), so the rise of the internal resistance of a cell cannot be controlled effectively.

[0010] If a lithium is included, since a content **** lithium will be emitted by charge, the oxidation number of nickel and cobalt will become large exceeding 3 and it is the same as having stated previously, a nickel oxide and cobalt oxide are limited to what does not contain a lithium because the internal resistance of a cell is raised on the contrary rather than an additive-free case.

[0011] That the addition of a nickel oxide and a cobalt oxide is regulated to 0.1-20-mol% to positive active material If it is not fully discovered and the addition effectiveness (effectiveness which works as catalyst poison and controls disassembly of the electrolytic solution) exceeds 20-mol % on the other hand less than [0.1 mol %], while the conductivity of these oxides will originate in a low thing and the internal resistance of a cell will rise It is because diffusion of the lithium in the positive electrode at the time of charge and discharge worsens, so charge-and-discharge effectiveness falls.

[0012] A nickel oxide and a cobalt oxide may be mixed and you may add. Also in this case, it is necessary to regulate those total amounts to the 100 mol section of positive active material within the limits of the 0.1-20-mol section (0.1-20-mol %).

[0013] As a nickel oxide, they are NiO, nickel 2O₃, and nickel 3O₄. It is illustrated as a typical thing and they are CoO and Co 3O₄ as a cobalt oxide. Although illustrated as a typical thing, they are NiO and Co 3O₄ especially. It is especially desirable.

[0014] The thing as a negative electrode which uses the lithium in this invention as a negative-electrode active material, were using the metal lithium and the lithium ion, and using occlusion, the alloy which may be emitted, or the carbon material as an electrode material is illustrated.

[0015] This invention is LiX nickel1-Y CoY OZ. When it uses as positive active material, it succeeds in controlling disassembly of the electrolytic solution used as a problem by adding a nickel oxide and/or a cobalt oxide to positive active material, having it, and improving the preservation property under the elevated temperature of a nonaqueous cell. So, it is possible to use especially various ingredients which are conventionally proposed as an object for nonaqueous cells about other members which constitute a cell, or are used, such as the electrolytic solution, without a limit.

[0016] as nonaqueous electrolyte -- the mixed solvent of organic solvents, such as ethylene carbonate, vinylene carbonate, and propylene carbonate, these, and low-boiling point solvents, such as dimethyl carbonate, diethyl carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, and ethoxy methoxyethane, -- LiPF₆, LiClO₄, and LiCF₃ SO₃ etc. -- the solution which 0.7-1.5M (a mol/liter) came out comparatively, and melted the solute is illustrated.

[0017]

[Function] In this invention, since a nickel oxide and/or a cobalt oxide work as catalyst poison in the decomposition reaction of the electrolytic solution, even if saved for a long period of time, it is hard to generate gas (even if it is in a rechargeable battery and saves in the condition after charge especially for a long period of time). For this reason, deformation stops being able to happen to the plate configuration of a positive electrode easily, and the rise of the internal resistance of a cell is controlled.

[0018]

[Example] It is possible to change this invention suitably in the range which is not limited to the following example at all and does not change the summary, and to carry out hereafter, although this invention is further explained to a detail based on an example.

[0019] (Example 1) The nonaqueous cell (this invention cell) of a flat mold was produced.

[0020] [Positive electrode] LiOH and nickel2 (OH) Co2 (OH) After mixing with a mortar by the mole ratio 2:1:1, this mixture is heat-treated by 750-degreeC under a dry air ambient atmosphere for 20 hours, and it is LiNi0.5 Co 0.5O₂. The positive active material shown was obtained. subsequently, this positive-active-material powder after grinding in an Ishikawa style stone mill mortar so that mean particle diameter may be set to 5 micrometers -- receiving -- nickel2 O₃ powder (the oxidation number of nickel: 3) -- 0.1-mol % -- addition mixing was carried out.

[0021] subsequently, the above nickel 2O₃ the positive-active-material powder which carried out addition mixing, the acetylene black as an electric conduction agent, and the polyvinylidene fluoride as a binder -- the weight ratio 90:6:4 -- mixing -- a positive electrode -- a mixture -- preparing -- this positive electrode -- a mixture -- 2 t/cm² After carrying out pressurization molding by the pressure disc-like [with a diameter of 20mm], it heat-treated by 250-degreeC for 2 hours, and the positive electrode was produced.

[0022] [Negative electrode] The rolled plate of the metal lithium which has predetermined thickness was pierced to disc-like [with a diameter of 20mm], and the negative electrode was produced.

[0023] [Nonaqueous electrolyte] Lithium perchlorate was melted at a rate of 1M (a mol/liter) to volume mixed solvents, such as propylene carbonate and 1 and 2-dimethoxyethane, and nonaqueous electrolyte was prepared to them.

[0024] [Production of a cell] this invention cell BA 1 of a flat mold was produced using the above positive/negative two poles and nonaqueous electrolyte (cell dimension : 3.0mm in the diameter of 24.0mm, thickness). In addition, as a separator, the fine porosity film made from polypropylene (hex TOSERA needs company make, trade name "Celgard") was used, and previous nonaqueous electrolyte was infiltrated into this.

[0025] Drawing 1 is the sectional view showing the produced this invention cell BA 1 typically, and this invention cell BA 1 shown in this drawing consists of the separator 3 which estranges mutually a positive electrode 1, a negative electrode 2, and these two electrodes 1 and 2, the positive-electrode can 4, the negative-electrode can 5, the positive-electrode charge collector 6, a negative-electrode charge collector 7, insulating packing 8 made from polypropylene, etc.

[0026] The positive electrode 1 and the negative electrode 2 are contained in the cell case where counter through the separator 3 which sank in and the positive/negative two-poles cans 4 and 5 form nonaqueous electrolyte. Through the positive-electrode charge collector 6, with the positive-electrode can 4, a negative electrode 2 can be connected to the negative-electrode can 5 through the negative-electrode charge collector 7, and a positive electrode 1 can take out now the chemical energy produced inside the cell to the exterior as electrical energy again from the both-ends child of the positive-electrode can 4 and the negative-electrode can 5.

[0027] (Examples 2-5) nickel 2O₃ to positive-active-material powder The positive electrode was produced like the above-mentioned example 1 except having made the powdered addition into 20-mol % 15-mol% ten-mol% five-mol%, respectively.

Subsequently, this invention cells BA2 (the addition of nickel2 O₃ powder: five-mol %), BA3 (the addition of 2Nickel3 powder: ten-mol %), BA4 (the addition of nickel2 O₃ powder: 15-mol %), and BA5 (the addition of nickel2 O₃ powder: 20-mol %) were produced like the example 1 except having used this positive electrode.

[0028] (Examples 6-10) nickel 2O₃ It replaces with powder and is nickel 3O₄. The positive electrode was produced like examples 1-5 except having used powder (the oxidation number of nickel: 2.67). It is made to be the same as that of an example 1 except having used these positive electrodes. Subsequently, this invention cell BA 6 (the addition of 3Nickel4 powder: 0.1-mol %) BA7 (the addition of nickel3 O₄ powder: five-mol %), BA8 (the addition of nickel3 O₄ powder: ten-mol %), BA9 (the addition of nickel3 O₄ powder: 15-mol %), and BA10 (the addition of nickel3 O₄ powder: 20-mol %) were produced.

[0029] (Examples 11-15) nickel<SUB>2O₃ The positive electrode was produced like examples 1-5 except having replaced with powder and having used CoO (the oxidation number of cobalt: 2) powder. Subsequently, this invention cells BA11 (the addition of CoO powder: 0.1-mol %), BA12 (the addition of CoO powder: five-mol %), BA13 (the addition of CoO powder: ten-mol %), BA14 (the addition of CoO powder: 15-mol %), and BA15 (the addition of CoO powder: 20-mol %) were produced like the example 1

except having used these positive electrodes.

[0030] (Example 1 of a comparison) It is nickel 2O₃ to positive-active-material powder. The positive electrode was produced like the example 1 except having not carried out addition mixing of the powder. Subsequently, the comparison cell BC 1 was produced like the example 1 except having used this positive electrode.

[0031] (Example 2 of a comparison) nickel 2O₃ to positive-active-material powder The positive electrode was produced like the example 1 except having made the powdered addition into 25-mol %. Subsequently, the comparison cell BC 2 was produced like the example 1 except having used this positive electrode.

[0032] (Example 3 of a comparison) nickel 3O₄ to positive-active-material powder The positive electrode was produced like the example 6 except having made the powdered addition into 25-mol %. Subsequently, the comparison cell BC 3 was produced like the example 1 except having used this positive electrode.

[0033] (Example 4 of a comparison) The positive electrode was produced like the example 11 except having made the addition of the CoO powder to positive-active-material powder into 25-mol %. Subsequently, the comparison cell BC 4 was produced like the example 1 except having used this positive electrode.

[0034] The class and addition of the nickel oxide powder added to positive-active-material powder in production of each positive electrode of this invention cells BA1-BA15 and the comparison cells BC1-BC4 or cobalt oxide powder are collectively shown in the next table 1.

[0035]

[Table 1]

電池	添加した酸化物 (酸化数)	添加量 (モル%)
BC1	なし	無添加
BA1	Ni ₂ O ₃ (3)	0.1
BA2	"	5
BA3	"	10
BA4	"	15
BA5	"	20
BC2	"	25
BA6	Ni ₂ O ₄ (2, 67)	0.1
BA7	"	5
BA8	"	10
BA9	"	15
BA10	"	20
BC3	"	25
BA11	CoO (2)	0.1
BA12	"	5
BA13	"	10
BA14	"	15
BA15	"	20
BC4	"	25

[0036] [Preservation property] After charging this invention cells BA1-BA15 and the comparison cells BC1-BC4, it saved for 30 days by 80-degreeC, and the preservation property of each cell was investigated. A result is shown in drawing 2. The R/C (%) of the internal resistance of a cell estimated the preservation property. The internal resistance of a cell was computed by the bottom type.

[0037] Internal resistance before R/C (%) =(internal resistance before the internal resistance-preservation after preservation) x100-/preservation of the internal resistance of a cell [0038] Drawing 2 is Graf who the R/C (%) of the internal resistance of a cell was taken along the axis of ordinate, and it took the addition (mol %) of a nickel oxide or a cobalt oxide along the axis of abscissa, and showed the preservation property of each cell, and as shown in this drawing, its R/C of the internal resistance of a cell is as high by the comparison cells BC1-BC4 as 100% or more to a thing with the R/C of the internal resistance of a cell as low by this invention cells BA1-BA15 as 50% or less. the nickel oxide or cobalt oxide with which the oxidation number of nickel and cobalt is three or less, and the rise of the internal resistance of the cell when saving at an elevated temperature does not contain a lithium in a crystal from this -- positive active material -- receiving -- 0.1-20-mol % -- by adding shows being controlled notably.

[0039] (Examples 16-20) nickel 2O₃ The positive electrode was produced like examples

1-5 except having replaced with powder and having used NiO (the oxidation number of nickel: 2) powder. Subsequently, this invention cells BA16 (the addition of NiO powder: 0.1-mol %), BA17 (the addition of NiO powder: five-mol %), BA18 (the addition of NiO powder: ten-mol %), BA19 (the addition of NiO powder: 15-mol %), and BA20 (the addition of NiO powder: 20-mol %) were produced like the example 1 except having used these positive electrodes.

[0040] (Examples 21-25) nickel 2O₃ It replaces with powder and they are NiO powder and Co 3O₄. The positive electrode was produced like examples 1-5 except having used equimolar mixture with powder (the oxidation number of cobalt: 2.67). It is made to be the same as that of an example 1 except having used these positive electrodes.

Subsequently, this invention cell BA 21 (the total addition of NiO powder and Co₃ O₄ powder: 0.1-mol %) BA22 (the total addition of both powder: five-mol %), BA23 (the total addition of both powder: ten-mol %), BA24 (the total addition of both powder: 15-mol %), and BA25 (the total addition: 20-mol %) were produced.

[0041] (Examples 26-30) nickel 2O₃ It replaces with powder and is Co 3O₄. The positive electrode was produced like examples 1-5 except having used powder. It is made to be the same as that of an example 1 except having used these positive electrodes.

Subsequently, this invention cell BA 26 (the addition of Co₃ O₄ powder: 0.1-mol %) BA27 (the addition of Co₃ O₄ powder: five-mol %), BA28 (the addition of Co₃ O₄ powder: ten-mol %), BA29 (the addition of Co₃ O₄ powder: 15-mol %), and BA30 (the addition of Co₃ O₄ powder: 20-mol %) were produced.

[0042] (Example 5 of a comparison) The positive electrode was produced like the example 16 except having made the addition of the NiO powder to positive-active-material powder into 25-mol %. Subsequently, the comparison cell BC 5 was produced like the example 1 except having used this positive electrode.

[0043] (Example 6 of a comparison) NiO powder and Co 3O₄ to positive-active-material powder The positive electrode was produced like the example 21 except having made the powdered total addition into 25-mol %. Subsequently, the comparison cell BC 6 was produced like the example 1 except having used this positive electrode.

[0044] (Example 7 of a comparison) Co 3O₄ to positive-active-material powder The positive electrode was produced like the example 26 except having made the powdered addition into 25-mol %. Subsequently, the comparison cell BC 7 was produced like the example 1 except having used this positive electrode.

[0045] The class and addition of the nickel oxide powder added to positive-active-material powder in production of each positive electrode of this invention cells BA16-BA30 and the comparison cells BC5-BC7 or cobalt oxide powder are collectively shown in the next table 2.

[0046]

[Table 2]

電池	添加した酸化物 (酸化数)	添加量 (モル%)
BA16	NiO(2)	0.1
BA17	"	5
BA18	"	10
BA19	"	15
BA20	"	20
BC5	"	25
BA21	NiO(2) + Co ₃ O ₄ (2.67) 1 : 1 (添加割合)	0.1
BA22	"	5
BA23	"	10
BA24	"	15
BA25	"	20
BC6	"	25
BA26	Co ₃ O ₄ (2.67)	0.1
BA27	"	5
BA28	"	10
BA29	"	15
BA30	"	20
BC7	"	25

[0047] [Preservation property] The preservation property of this invention cells BA16-BA30 and the comparison cells BC5-BC7 was investigated like the point. A result is shown in drawing 3. In addition, in drawing 3, the result (it posts from drawing 2) of the comparison cell BC 1 is also shown for comparative facilities.

[0048] Drawing 3 is Graf who the R/C (%) of the internal resistance of a cell was taken along the axis of ordinate, and it took the addition (mol %) of a nickel oxide or a cobalt oxide along the axis of abscissa, and showed the preservation property of each cell. However, if it is in this invention cells 21-BA 25 and the comparison cell BC 6, an axis of abscissa shows the total addition of a nickel oxide and a cobalt oxide. As shown in drawing 3, by the comparison cells BC5-BC7, the R/C of the internal resistance of a cell is as high as 100% or more to a thing with the R/C of the internal resistance of a cell as low by this invention cells BA16-BA30 as 50% or less. the nickel oxide powder and/or cobalt oxide powder with which the oxidation number of nickel and cobalt is three or less, and the rise of the internal resistance of the cell resulting from disassembly of the electrolytic solution at the time of saving at an elevated temperature does not contain a lithium in a crystal from this -- positive-active-material powder -- receiving -- 0.1-20-mol % -- by adding shows being controlled notably.

[0049] (Examples 8-10 of a comparison) nickel 2O₃ It replaces with powder and is NiO₂. The positive electrode was produced like examples 1-3 except having used powder (the

oxidation number of nickel: 4). Subsequently, the comparison cells BC8 (the addition of NiO₂ powder: 0.1-mol %), BC9 (the addition of NiO₂ powder: five-mol %), and BC10 (the addition of NiO₂ powder: ten-mol %) were produced like the example 1 except having used these positive electrodes.

[0050] (Examples 11-13 of a comparison) nickel 2O₃ It replaces with powder and is CoO₂. The positive electrode was produced like examples 1-3 except having used powder (the oxidation number of cobalt: 4). Subsequently, the comparison cells BC11 (the addition of CoO₂ powder: 0.1-mol %), BC12 (the addition of CoO₂ powder: five-mol %), and BC13 (the addition of CoO₂ powder: ten-mol %) were produced like the example 1 except having used these positive electrodes.

[0051] [Preservation property] The preservation property of the comparison cells BC8-BC13 was investigated like the point. A result is shown in Table 3.

[0052]

[Table 3]

電池	添加した酸化物 (酸化数)	添加量 (モル%)	内部抵抗の上昇率 (%)
B C 8	N i O ₂ (4)	0. 1	8 0
B C 9	"	5	1 0 0
B C 1 0	"	1 0	1 2 0
B C 1 1	C o O ₂ (4)	0. 1	9 0
B C 1 2	"	5	1 1 0
B C 1 3	"	1 0	1 3 0

[0053] As shown in Table 3, the R/C of the internal resistance of the comparison cells BC8-BC13 is as high as 80% or more. Even if it adds the cobalt oxide with which the oxidation number of the nickel oxide with which the oxidation number of nickel exceeds 3, or cobalt exceeds 3 from this to positive active material, it turns out that disassembly of the electrolytic solution cannot fully be controlled.

[0054] Although the case where this invention was applied to a flat mold cell was mentioned as the example and the above-stated example explained it, especially a limit does not have this invention in a cell configuration, and it can apply cylindrical, a square shape, etc. to other various nonaqueous primary cells or nonaqueous rechargeable batteries of a configuration.

[0055] In addition, although it thought that this invention persons mainly depended generating of the gas in a fuel cell subsystem on decomposition of nonaqueous electrolyte, generating of the gas by disassembly of a binder is also considered. If improvement in the preservation property by this invention is because generating of the latter gas was also controlled, it is thought that application not only to a liquid electrolyte cell but a solid electrolyte cell is possible for this invention.

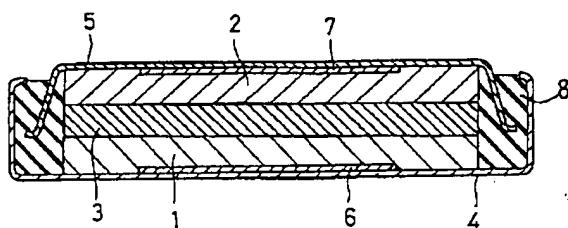
[0056]

[Effect of the Invention] Since disassembly of the electrolytic solution at the time of elevated-temperature preservation is controlled by adding a nickel oxide and/or a cobalt oxide to positive active material, the rise of the internal resistance of a cell is small and

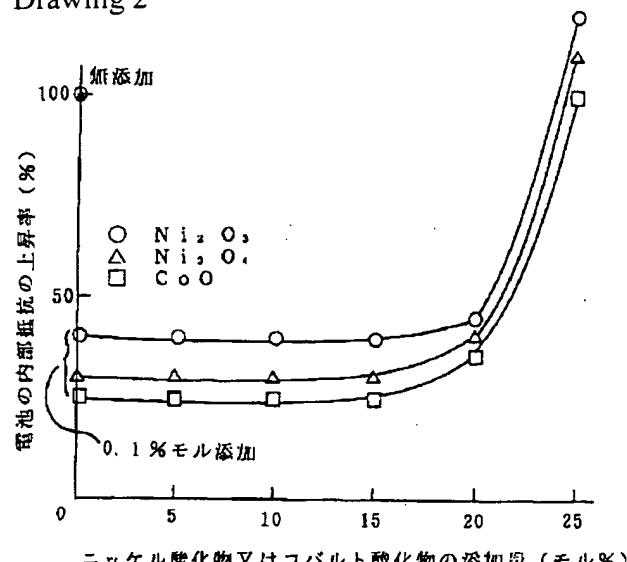
excellent in a preservation property.

Drawing 1

B A 1



Drawing 2



Drawing 3

